# Gas/Liquid Membranes For Natural Gas Upgrading

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Principal Author: Howard S. Meyer, Principal Manager, Gas Processing Research
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To

Anthony M. Zammerilli
Project Manager
National Energy Technology Laboratory
P.O. Box 880
3610 Collins Ferry Road
Morgantown, WV 26507

By

GAS TECHNOLOGY INSTITUTE
1700 South Mount Prospect
Des Plaines, IL 60018-1804

## *DISCLAIMER*

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## ABSTRACT

Efforts this quarter have concentrated on field site selection. ChevronTexaco has signed a contract with Kværner process Systems for the 50 MM scf/d dehydration skid at their Headlee Gas Plant in Odessa, TX for a commercial-scale test. This will allow the test to go forth. A new test schedule was established with testing beyond the existing contract completion date. Potting and module materials testing continued. Construction of the bench-scale equipment was started. Additional funding to support the test was obtained through a contract with Research Partnership for Secure Energy for America.


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## INTRODUCTION

Gas Technology Institute (GTI) is conducting this research program whose objective is to develop gas/liquid membranes for natural gas upgrading to assist DOE in achieving their goal of developing novel methods of upgrading low quality natural gas to meet pipeline specifications.

Kværner Process Systems (KPS) and W. L. Gore & Associates (GORE) gas/liquid membrane contactors are based on expanded polytetrafluoroethylene (ePTFE) membranes acting as the contacting barrier between the contaminated gas stream and the absorbing liquid. These resilient membranes provide much greater surface area for transfer than other tower internals, with packing densities five to ten times greater, resulting in equipment 50 – 70% smaller and lower weight for the same treating service.

The scope of the research program is to (1) build and install a laboratory- and a field-scale gas/liquid membrane absorber; (2) operate the units with a low quality natural gas feed stream for sufficient time to verify the simulation model of the contactors and to project membrane life in this severe service; and (3) conducted an economic evaluation, based on the data, to quantify the impact of the technology. Chevron, one of the major producers of natural gas, has offered to host the test at a gas treating plant. KPS will use their position as a recognized leader in the construction of commercial amine plants for building the unit along with GORE providing the membranes. GTI will provide operator and data collection support during lab- and field-testing to assure proper analytical procedures are used. Kværner and GTI will perform the final economic evaluation. GTI will provide project management and be responsible for reporting and interactions with DOE on this project.

## *EXECUTIVE SUMMARY*

The cofunding agreement with ChevronTexaco continues under discussion. ChevronTexaco's Chinchaga Gas Plant in Alberta, Canada will not be increasing capacity as planned. Since they do not have a commercial need for the contactor, they have withdrawn that site and are seeking another suitable location. We continue seeking alternative hosts and sites as a backup. A meeting was held with ChevronTexaco in Denver last quarter, 2002 to identify potential locations. Most of their needs are outside the North American market.

Early in 2003, ChevronTexaco identified a potential test site in West Texas. The application here is for a full-scale dehydration unit, similar in size as originally proposed, but for a different natural gas processing application. A meeting was held with ChevronTexaco, GTI and KPS at the Headlee Gas Plant in Odessa, TX, to investigate testing, contract terms, schedules, and responsibilities. A design review meeting (originally planned as a HazOp review, but served more as design) was conducted at KPS offices in Houston, TX during the third quarter, 2003. For this analysis, focus was on issues directly affecting the planned tie-ins.

A meeting was held with Tony Zammerilli, DOE Project Manager, in Morgantown, PA to review status of the project during the third quarter, 2003. This project has been delayed due to the time required to secure an appropriate site after the originally proposed site became unavailable. GTI has slowed down the project so that the original funding would be available. However, the cost of the test has increased. KPS and ChevronTexaco have increased their planned co-funding, but there is still a gap. He indicated that there is no out-year funding for Gas Processing projects in the DOE budget. He indicated that he would be responsive to reasonable changes in the program direction to help ensure the test occurs, within the bounds of the contract. The Contract Administrators must approve any changes to schedule and costs.

GTI was awarded a research contract from Research Partnership for Secure Energy for America (RPSEA) that will provide cofunding for this project. The objective of the proposed project is to develop gas/liquid membrane contactors for deep, offshore processing of natural gas to decrease the overall cost to bring these valuable reserves to the market. The scope of work for this program is to design, construct, install, and operate a 50 million standard cubic feet per day commercial-scale dehydration absorber in a gas plant environment at 900 psi, in conjunction with the DOE Project. This

absorber will be designed to offshore specifications so that it can be moved to platform operations, if successfully demonstrated. Prior to installation, a novel membrane protection system will be tested in the laboratory to study response time under simulated failure modes. An engineering research study will design the dehydration system for a typical deepwater, offshore Gulf of Mexico application and then conceptualize a subsea installation utilizing the technology. Work will begin first quarter, 2004.

## *EXPERIMENTAL*

### ChevronTexaco module:

A HazOp meeting was held at the Headlee Gas Plant in Odessa, TX this quarter. The current flowsheet is shown Figure 1.

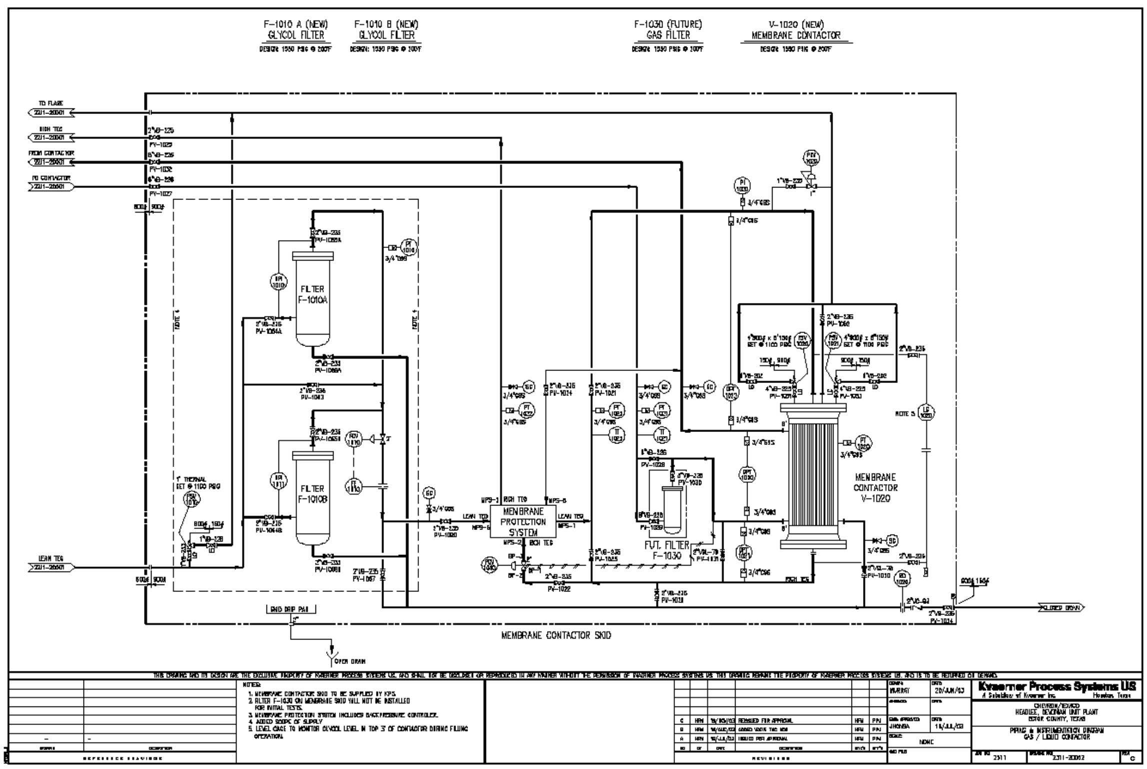


**Figure 1 Headlee Test Skid P&ID**

GTI will be responsible for the collection of data, and will install a separate analytical/office trailer at the site. The trailer will be equipped with the needed analytical equipment and data collecting systems. GTI will also supply (to be borrowed for testing period) an on-line Ametek moisture analyzer for dry gas analysis (water in dry gas). The wet gas water content will be calculated and verified by a water mass balance (dry and wet gas and lean and rich TEG).

The sampling plan and procedures was prepared this quarter for review and is included as Appendix A of this quarterly report.

### Potting Testing

The present potting material has its limitation in the casting of larger diameters due to high exothermic peak and subsequent cracking of cured material. Therefore, a search for a new thermosetting material was initiated.

Chemical immersion test:

The most common gas treatment absorbents were picked out for the test where resin samples (including membrane and spacer) are exposed for 24 weeks at 60°C. The following solvents were chosen:

- TEG
- MEA
- MDEA
- aMDEA (highly activated from BASF)
- Morphysorb
- Selexol/Genosorb

As a measure for chemical resistance, the adhesion between membrane/PTFE and resin was chosen in addition to swelling of sample. Chemical resistance test will be performed after 6, 12, and 24 weeks.

Parallel to the chemical testing, the following activities will be performed:

- potting simulations, i.e. study of the rheological behavior of approx. 3 kg samples of the various resins in a plexiglass mould of length/diameter 720 mm which is filled with membrane sheets and spacer material
- building dummies of the full size diameter and thickness (approx. 40 kg resin), both to see the rheological behavior and the curing performance in full scale
- identify the new potting material.

### Laboratory Testing

Summary

Design efforts have been initiated towards fabrication of the facilities to perform the next phase of gas-liquid membrane tests. A first-pass at the major process flow has been formulated, including a simplified P&ID and a Design Basis. Mechanical overviews of the pressure vessel are presented, to facilitate evaluation of options for fabrication of the membrane module. Review and comments have been received from KPS to allow movement to the next stages of implementation.

Introduction

The approach is (1) to modify an existing high-pressure facility, within an enclosure in the south west corner of Laboratory 636 at Des Plaines and (2) to utilize the high-pressure compressor / circulation system, which has been installed for the scavenger test rig, to supply the primary gas requirements.

As these facilities are upgrades for the gas-liquid membrane program, existing equipment will be left in place as much as possible in the facilities, which will facilitate future flexibility for comparing the gas/liquid membrane with conventional contactors.

The current plan is to conduct primarily sweetening operations, in a sequence as follows

1— Carbon dioxide removal (from a nitrogen-based stream)

2--- Hydrogen sulfide removal (also from a nitrogen-based stream)

3--- Other components, such as water (in a nitrogen stream)

Process Flow

The proposed process flow is shown in the simplified P&ID in Figure 2. Major vessels have been included, as well as most of the process piping, with line sizes. However, only primary process controllers, such as flow and pressure controllers have been included at this point. Items such as line or vessel heaters, safety and interlock systems, a membrane-protection system, and other details will be added at a later stage.

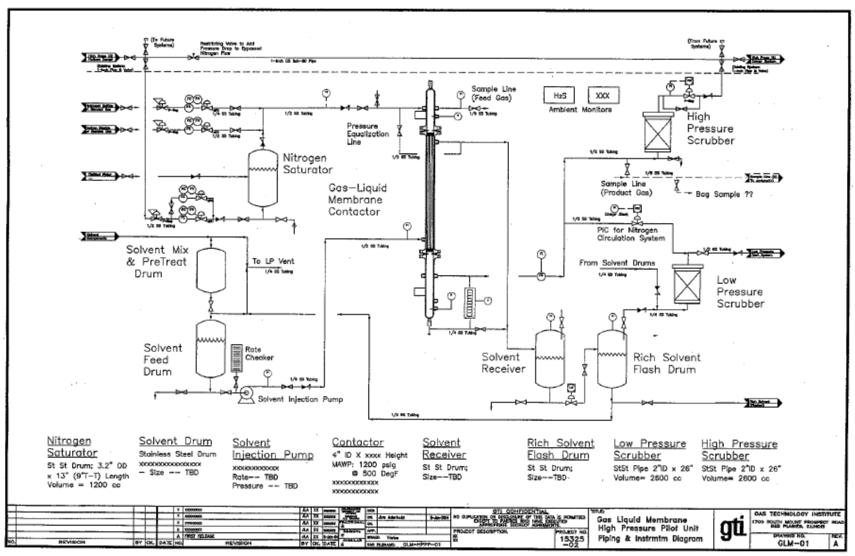


**Figure 2 Proposed Laboratory Test Unit P&ID**

The center of the experiment system will be the membrane module, which will contain tubes of membranes enclosed in a pressure vessel. For this first pass, we have assumed that the membrane module can be mounted vertically. The feed gas stream would be passed down through the membrane tubes. It is assumed that the solvent will be flowing upward on the shell side of the membrane module.

The bulk of the gas flow will be nitrogen and will come from the circulating compressor system, which was installed recently by the Gas Processing team at GTI for the "scavenging" test stand. A connection to this source of high-pressure nitrogen is currently being implemented. There are two features of this system, which need to be mentioned. First, there is currently no high-pressure make up capability for the compressor system (other than bottled gases), so the high-pressure nitrogen must be cleaned up at the gas-liquid membrane test facility and recycled back to the compressor suction. Second, the compressor is a positive-displacement machine, so the flow rate range is relatively fixed. Since the flow rate is substantially more than that desired for the gas-liquid membrane program, a bypass will be included as the connection is made from the compressor system to the gas-liquid membrane facility, so that most of the high-pressure nitrogen stream is recycled back to the compressor suction. Only a slip stream of the overall high-pressure nitrogen circulation is routed to the gas-liquid membrane unit.

The existing system contains parallel mass flow controllers for the nitrogen feed, which can each give about 1000 scfh at 1000 psig. There also exists a mass flow controller (for lower flow rates) to feed concentrated hydrogen sulfide blends into the feed gas stream. Another mass flow controller will be added to deliver concentrated carbon dioxide for studies at about 800 psig. The existing system has a bubbler ("Nitrogen Saturator") in line for the nitrogen feed stream so that water can be added, if it is necessary to humidify the feed gas.

<u>Construction</u>

Progress has been made this quarter preparing the experimental lab unit. As can be seen in Figure 3, a majority of the hard piping and vessels are installed. A meeting was held with KPS this quarter on the design of the experimental gas/liquid membrane contactor. The first design was to incorporate the membranes within the column spool pieces. This may not be feasible, as it would result in excess residence time in the remained of the column. GTI has proposed a column design based on tubing and Swageloc® fittings that is being evaluated.


**Figure 3 GTI Absorption Lab Unit**

## *RESULTS AND DISCUSSION*

### Chemical immersion in TEG – Second Test Series:

The final tests and evaluations after 26-27 weeks in TEG (and other chemicals) were finished at the end of the quarter. Results will be presented next quarter.

### Potting simulation tests

On the background of chemical immersion tests, peeling tests, viscosity and exothermic peak, two additional potting systems have been chosen for potting simulation tests and dummy-tests. Both new systems chosen from the Test Series 2 performed very well in the potting simulation test (leveling behavior and adhesion to the membranes).

To try to optimize the present potting system, different tests have been done in the potting simulation mould. The temperature of the resin and temperature of the equipment have been varied while injecting the resin into the mould. The conclusion from these tests is that higher temperatures of the resin and equipment will not improve the levelling of the resin in the pot due to increased rate of chemical conversion (increased reaction rate predominates decreased viscosity).

### Dummy tests

**Test Material 1:** The pure resin system (without membranes and spacers) was potted in a full scale mould (720 mm) to check the behavior of the material while curing (tensions, cracks, temperature rise). The cured sample was cut in slices and checked for defects. No cracks or pores or other defects was detected which indicates a controlled curing reaction. The exothermic peak was slightly lower than in the corresponding test with the reference system.

A half dummy, filled with membranes and spacers, was made by injection of approx. 20 kg of epoxy resin into the mould. The Test Material 1 demonstrated an excellent leveling behavior, better than the reference system.

**Test Material 2:** The pure resin system (without membranes and spacers) was potted in a full scale mould (720 mm) as for previous systems. The sample (approx. 50 kg) seemed to be OK after curing and also after post-curing (24 hours at 80°C). During the cooling process from 80°C to room temperature, a few cracks appeared in the sample. In addition, the resin in the bottom rather soft, not fully cured. It was decided to repeat the test, because the soft resin could indicate insufficient mixing of the resin and hardener.

No soft areas were registered in the repeated test, but cracks appeared once again. One of the reasons for these cracks could be that this system is not filled, leading to excessive tension in the resin matrix. We decided to exclude this system for potting purposes.

## *CONCLUSION*

A practical upper temperature limit for potting has been identified. The potting simulation testing has identified Test Material 1 to be better than the reference material. Test Material 2 was found to be unacceptable.

## *REFERENCES*

None

# Appendix A

**Field Sampling and Analytical Plan**

**for**

**FIELD DEMONSTRATION OF KVÆRNER PROCESS SYSTEMS' MEMBRANE CONTACTOR TECHNOLOGY AT CHEVRONTEXACO'S HEADLEE PLANT**

**GAS TECHNOLOGY INSTITUTE**

**1700 South Mount Prospect**

**Des Plaines, IL 60018**

**<u>Rev. 0</u>**

**March 20, 2004**

# Gas/Liquid Membranes For Natural Gas Upgrading

GTI Project 61147      Contract Number: DE-FC26-01NT41227

### 1.0 Introduction

The Gas Technology Institute (GTI), on behalf of Kværner Process Systems (KPS), will perform the work described in this Field Sampling and Analytical Plan (FSAP) as a part of overall KPS objective of demonstrating Gas-Liquid Contactor technology at ChevronTexaco's Headlee plant site.

## *2.0 Project Overview*

Since 1992, KPS and their technology partner, W.L. Gore & Associates GmbH (GORE), have been working on the development of Gas-Liquid contactor technology for removal of water, hydrogen sulfide, and carbon dioxide from natural gas. Within last few years, GTI has participated with KPS for field-testing of gas-liquid membranes both at Fandango test site in Texas and Duke Field Services near Denver, CO.

To advance the Gas-Liquid contactor technology further into market place, KPS and ChevronTexaco (CT) have entered into agreement to test the gas-liquid gas membrane contactor at CT's Headlee Gas Plant facility. This agreement calls for two sets of operations, performance testing and endurance testing, as specified in the experimental plan. During the performance testing, GTI and KPS personnel will be on-site operating, sampling and performing analyses. During endurance testing, plant personnel will collect samples and ship them to GTI as specified in this plan.

### 3.0 Sampling Streams and Frequency

Table 1 shows the sampling streams for the Gas-Liquid Contactor field test program. However, frequency schedule and sampling needs will be re-evaluated before start of field test program and, if needed, a revised sampling plan will be provided to the all parties concerned with this project.

**Table 1. Sampling Streams and Frequency**

| Sampling Stream | Performance Testing Frequency | Endurance Testing Frequency | Method |
|---|---|---|---|
| Wet Natural Gas | Once a day by GTI/KPS staff | Once a week by plant personnel | Stain tube |
| Dry Natural Gas | Online | Online | Ametek Analyzer |
| Lean | Every four hours by | Once a week by plant | Karl Fischer Water |

| | | | |
|---|---|---|---|
| Glycol Water Content | GTI/KPS staff | personnel | Titration onsite when GTI/KPS staff present and at GTI all other times |
| Rich Glycol Water Content | Every four hours by GTI/KPS staff | Once a week by plant personnel | Karl Fischer Water Titration onsite when GTI/KPS staff present and at GTI all other times |
| Knockout liquids | Whenever required | Whenever required | GC/ Karl Fischer Water Titration onsite when GTI/KPS staff present and at GTI all other times |

### 4.0 Sampling And Analytical Activities

This section describes the sampling techniques and analytical methods that will be used during the gas-liquid membrane contactor field test program. The inlet natural gas will be fully characterized for inert, acid gases and hydrocarbons at the beginning of each test phase. The remainder of this section describes the sampling methods first, followed by a discussion of the analytical methods

### 4.1 Sampling Methods

Each method of collecting natural gas and liquid samples is described below.

#### 4.1.1 Grab Samples for Characterization

For inlet natural gas samples to be analyzed at an off-site GTI laboratory, pressurized stainless-steel gas cylinders will be used for sample collection. The gas cylinders will be filled to the process pressure and immediately shipped for analysis.

#### 4.1.2 Stain-Tube Analysis

Tedlar bags will be used to collect samples for stain-tube analysis. Stain-tube measurement involves drawing a metered volume of gas through a glass tube containing precise amounts of detecting reagents. Chemical agents in the detector tubes react with the sample gas and a color stain indicates the gas concentration. Gas detector tubes typically contain colorimetric reagents adsorbed on fine grain silica gel, activated alumina, or other adsorbing media.

#### 4.1.3 Knockout Liquids Sampling Method

These liquids will be collected in 40 mL vials. Prior to collecting the sample, the sample valve will be opened and allowed to purge for a few seconds. The relative amount of condensate in the separator liquids will be noted when collecting knockout samples.

#### 4.1.4 Glycol Liquids Sampling Method

These liquids will be collected in 40 mL vials. Prior to collecting the sample, the sample valve will be opened and allowed to purge for a few seconds.

### 4.2 Analytical Methods

This section describes the analytical methods for water vapor, hydrocarbons and fixed gases, and knockout liquids.

#### 4.2.1 Natural Gas Analysis---Water Content of Natural Gas

##### *4.2.1.1 Wet Natural Gas*

GTI is currently investigating the option of a simple analytical field method to be used for the wet gas stream, such as use of stain tubes. The wet, feed gas should be saturated with water under normal operating conditions. Since it is important to know the inlet water, stain tubes will be used to check the water content on a daily basis during the performance testing and weekly during the endurance testing. ASTM method-D 4888-88 will be used for measurement of water content in natural gas. The water content of the wet gas will be calculated based on water saturation curves. A gas sample will also be shipped to GTI for further analysis.

##### *4.2.1.2 Dry Natural Gas (Gas-Liquid Membrane Contactor Outlet) Analysis*

The water content in dry gas will be monitored continuously using a dedicated Ametek 3050-OLV moisture analyzer on loan to the project by GTI. This analyzer has its own calibration gas (50 ppmv) and will be periodically checked to verify calibration. In addition to this, there will be a separate $N_2$ cylinder next to the analyzer to be used as a reference gas and verify the operation of the analyzer if needed. Figure 1 shows the analyzer skid and associated gas and electrical connections.

The analyzer requires between 150 – 1000 sccm of gas flow through the detector cell. In addition the sample conditioning section requires vapor bypass and GENIE filter vent flows to prevent any liquids or condensate to enter the analyzer. The total vent flow (vapor bypass + GENIE vent) will be maximum 1500 sccm. The analyzer will be connected to a laptop computer, also on loan from GTI, through an RS-485 serial connection and collect data periodically, which will be stored in the computer. There is also a 4-20 mA analog signal output for connection to the PLC system. Sample in and outlet/vent lines are ¼" stainless steel tubing. Voltage and power requirements are 120 Vac, 50/60Hz, 200W max. including the heated pressure regulator.

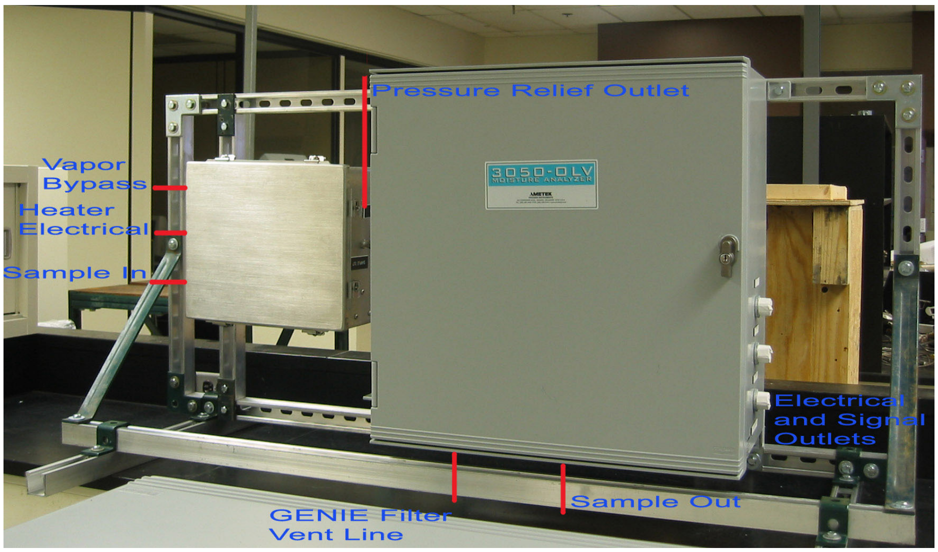


**Figure 1. Ametek 3050-OLV Moisture Analyzer**

### 4.2.2 Gas sample points (Wet and Dry gas)

Two sample points per gas stream are required, one to be connected to the online analyzer, the other one to take spot samples. Each sample point should have a correctly positioned sample probe and a separator with a pressure gauge. Gas sample points should be located on the top of a horizontal line, away from bends and at the middle third portion of the line whenever possible. Care should be taken to choose a sample location such that the Ametek moisture analyzer will be located higher than the sample probe to prevent any dips or low spots.

Also it is preferred to have as short of a distance as possible between the sample probe and the analyzer. Figure 2 shows a typical gas sample probe installation.

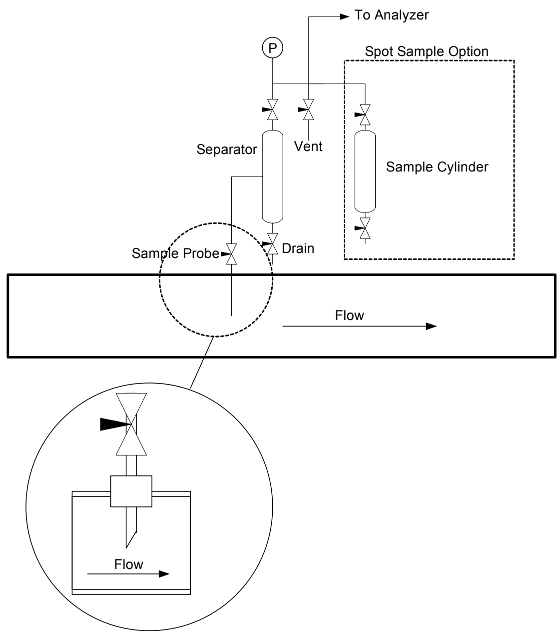


**Figure 2. Gas Sampling Point with Probe and Optional Spot Sampling Cylinder**

Welker Engineering supplies a sample probe (SP-2 Standard Probe) for natural gas sampling purposes. Probe is 316 stainless steel, ½" or ¾" NPT pipe connection with outlet valve. Standard valve outlet size is ¼" NPT. A commercially available separator can be used or if needed one can be made as shown on Figure 3.

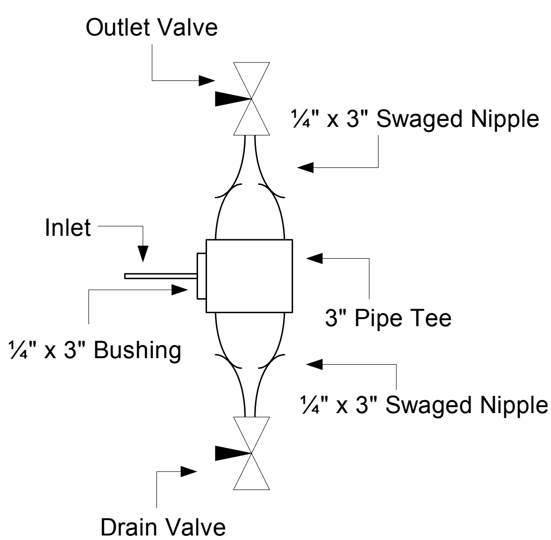


**Figure 3. Gas Sampling Separator Example**

### 4.2.3 Hydrocarbons and Fixed Gases

The natural gas sample will be analyzed by GTI at their Des Plains location. Standard GPA analysis methods based on gas chromatography with flame ionization detection will be used for a complete characterization of $C_1$ - $C_6$+ compounds. Fixed gases (carbon dioxide, methane, nitrogen, and oxygen) will be determined using gas chromatography with thermal conductivity detection (TCD).

### 4.2.4 Knockout Liquids Analyses

Samples of the knockout vessel liquids and any other liquids collected from the skid unit will be analyzed for its content at their Des Plaines location.

### *4.2.5 Glycol Solids Content*

Total Suspended Solids—Total Suspended Solids (TSS) in glycol stream will be determined using EPA Method 160.2, if needed, at their Des Plaines location. A measured aliquot of sample is filtered through a fine glass fiber filter. The mass of solids per liquid volume is the TSS.

### *4.2.6 Lean and Rich Glycol Analysis*

The water content of lean and rich glycol samples will be analyzed using a Metrohm Automatic Karl Fisher Titrator. A set of lean and rich glycol samples will be collected in 40 mL glass vials every 4 hours during GTI presence and analyzed at the lab space provided. When GTI is not present, samples will be collected once a week and shipped to GTI for analysis. Figure 4 shows the Metrohm Karl Fisher titrator and its associated parts. The required reagent and methanol will be provided by GTI and will be stored in the lab space. The glycol samples collected will be set to GTI for storage and further testing every 14 days.

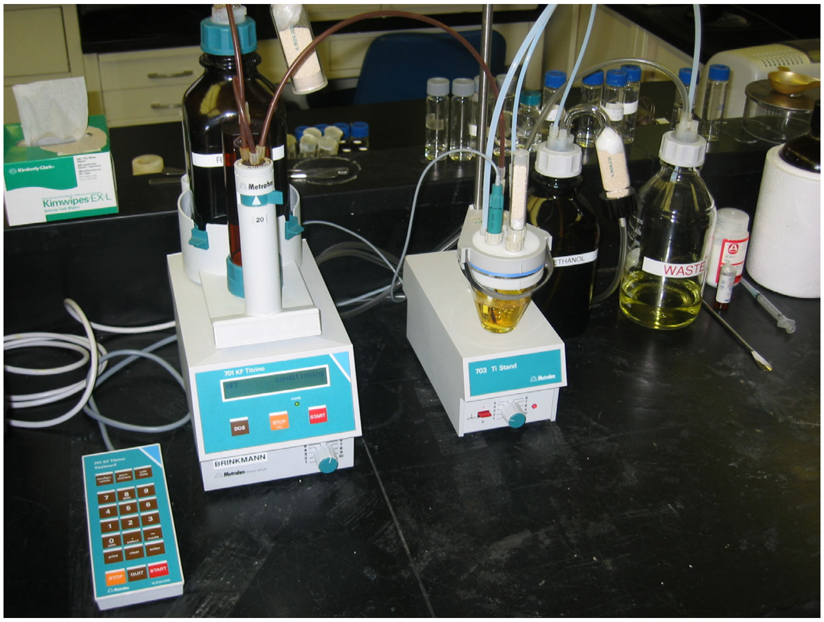

**Figure 4. Metrohm Automatic Karl Fisher Titrator**

### 4.2.6.1 Karl Fischer Water Analysis Procedure

1. Before you begin make sure that green "cond." Led is on and not blinking.
2. Using a clean, new syringe withdraw about 0.6 mL of sample
3. Press "Start" once.
4. Put syringe on balance and press "Re-zero" until you see a constant "0.000x" reading.
5. Inject the sample into reaction vessel using septum port
6. Before pulling the syringe out withdraw some air into the syringe.
7. Put the syringe back on the balance.
8. Type in the sample weight using keypad and press "Enter".
9. Water concentration in weight % will be displayed in about one minute.
10. Record sample size, KFR volume and water %.

### 4.2.6.2 Liquid sample points (Rich and Lean Glycol)

Sample point location should be selected to represent the stream as accurately as possible. The middle third portion of a horizontal line should be chosen if possible. Care should be taken not to take samples from stagnant or dead-end sources. A ¼" block valve followed by a needle valve is sufficient. A length of ¼" stainless steel tubing allows for easy transfer of sample to collection container. Figure 5 shows a typical liquid sample point.

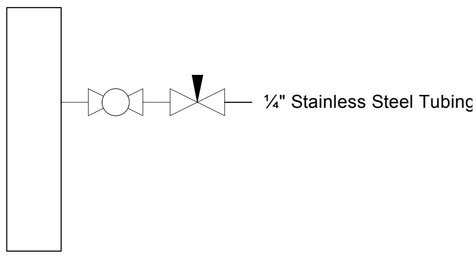


**Figure 5. Liquid Sample Point**

## 5.0 Sample Documentation: Collection, Storage and Labeling

All collected samples will be recorded in a logbook and labeled with sample name, date, and time collected. The test conditions such as gas flow rates, temperatures, and pressures will be recorded manually in addition to online data acquisition system. Samples will be identified properly with field sample labels. All samples that are collected will be stored as per standard laboratory practices and solvents will be stored in a refrigerator as needed.

## 6.0 Material Safety Data Sheets

All material safety datasheets for all chemicals used will be made available at GTI/KPS analytical trailer unit.

## 7.0 Sample Disposal Procedures

Not required. All liquid and gas samples that will be collected will be shipped to GTI. In case of sample disposal at site is needed, standard host site disposal regulations will be followed.

## 8.0 Sample Shipping

All samples collected for analytical testing at GTI, Des Plains laboratory will be shipped overnight (e.g., Federal Express). All samples will be shipped in accordance with state and federal shipping rules and regulations.